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# (54) Drilling fluid emulsion composition

(57) A drilling fluid composition in which the continuous phase of an emulsion comprises a linear alkyl benzene. Preferably the alkyl group has from 4 to 40 carbon atoms.

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"<u>Drilling Fluid</u>"

This invention relates to drilling fluid for use in the drilling of wells.

Drilling fluids are circulated down a wellbore during well drilling operations. The fluid is usually pumped down a central drillstring, passes through the drill bit into the wellbore and then returns to the surface. The fluid is then recovered, solid materials extracted, processed and reused.

Drilling fluids are required to remove rock cuttings generated during the boring process, to lubricate and cool the drill bit and maintain the integrity of the hole. Physical properties of the drilling fluid such as viscosity, density, salinity and filtrate loss may be modified by chemical addition as necessary.

One major problem which occurs in the use of water based drilling fluids is the hydration of rock being drilled; this is particularly acute when the interval contains clays and shales. These materials exhibit a great affinity for water and adsorption leads to swelling of the rock with resultant stresses leading to

collapse of the borehole or loss of structure.

Such failures lead to wellbore expansion, stuck pipe, excessive rheology, and general drilling problems.

A second problem with water based drilling fluids which is particularly prevalent in the North Sea is the drilling of so called "salt stringers ". These intervals comprise regions of high concentrations of water soluble salts such as sodium, magnesium and potassium chloride which will dissolve in the drilling fluid and lead to hole enlargement, washout and general failure of the wellbore.

One solution to the above problems has been the use of so called "salt saturated" solutions in which a soluble salt, usually sodium chloride, is dissolved at maximum concentration in the aqueous medium and used as the drilling fluid base. Such solutions limit shale hydration and prevent further dissolution of drilled salts into the fluid.

However, salt saturated solutions are expensive, have limitations on the density range which may be used and limit the number of additives which may be used to control the properties of the drilling fluid.

A second and more widely applied solution involves the use of oil based drilling fluids which are usually formulated with mineral oils. These fluids comprise a salt-containing aqueous phase which is tightly emulsified into an external oil phase by the use of suitable surfactants.

Oil based drilling fluids therefore present to the

surface of drilled rocks an inert oil phase which will not hydrate shale nor dissolve salt. Further, cuttings recovered from oil based fluids are covered with a thin film of oil which prevent hydration and breakage.

Oil based drilling fluids have a much wider range of density, rheology, thermal stability and application than salt saturated or water based fluids and are widely used.

However, disposal of rock cuttings which contain a significant proportion of water insoluble oil, especially by disposal through marine dumping at the drill site, is becoming environmentally unacceptable.

In attempts to upgrade the performance of water based fluids further additives have been used to attempt to control shale hydration, for example potassium chloride, polyacrylamide, polyglycerols, carboxymethyl derivatives, gilsonite, calcium chloride and sodium silicate. However, none of these systems have proved to match the performance of oil based fluids and importantly have minimal effect in preventing solution of salt sections.

There exists a need for an environmentally acceptable alternative to oil based drilling fluid which exhibits control of both shale hydration and salt dissolution and which may be used over the density range covered by oil based fluids.

Currently-used oil based drilling fluids are described as "low toxicity" by virtue of the highly refined nature of the base oils which contain only a small percentage of aromatic compounds which can be harmful

to marine life or to the product handler. However, such fluids are very poorly degraded and will remain as a persistent contaminant at disposal sites for many years.

"Low toxicity" oils are produced by a series of fractionation and occasionally solvent extraction/precipitation processes from crude oils and hence contain a broad range of molecular structures only a small number of which are biodegradable.

However, hydrocarbons having similar structures to mineral oil may be prepared synthetically by polymerisation of ethylene or other unsaturated gases and liquids in manufacturing processes such as the Shell higher olefins process (SHOP). The resultant polyalphaolefins (PAO) are high purity compounds which because of the linear structure are highly biodegradable. Such a property would make a highly desirable alternative fluid to conventional mineral oil based drilling fluids.

However, another desirable property of the oil component of an oil based drilling fluid is that the oil should have a high flash point to ensure safety in use and a low freezing point to enable liquid handling under the low temperatures experienced during winter use or in low temperature regions of the world.

The flash point of a polyalphaolefin increases as the molecular weight increases but unfortunately the freezing point also rapidly increases such that liquid handling becomes difficult.

In addition polyalphaolefins contain a reactive

unsaturate terminal grouping which is prone to oxidation, polymerisation and undesirable reactions which can lead to a change in the physical properties of the fluid and could cause problems during the drilling process.

Other highly refined mineral oils such as liquid paraffins or polyalphaolefins stabilised by hydrogenation to yield liquid paraffins also suffer from the problem of high freezing point in high flash point fractions.

According to the present invention there is provided drilling fluid comprising an emulsion whose continuous phase comprises a linear alkyl benzene (LAB).

The LAB is selected to replace the mineral oil content of conventional oil based drilling fluids in which the oil phase may consist of napththenic, paraffinic and aromatic oils such as diesel, refined base oils, liquid paraffins and polyalphaolefins.

Linear alkyl benzenes provide a high flash point, low freezing point, stable liquid of good biodegradability which can be advantageously used to replace mineral oil in drilling fluid.

The resultant drilling fluid may be used to replace conventional "clean oil" drilling muds but is inherently biodegradable and may be treated or disposed of safely to the surrounding environment.

In addition the replacement of paraffinic "clean oil" by a linear alkyl benzene considerably increases the polarity of the drilling fluid oil phase such that

improved surfactant, emulsion and gellant characteristics are obtained from mud additives designed to effect the mud emulsion and convey suitable rheology to the system.

The structure of the linear alkyl benzene used as the hydrocarbon phase of the drilling fluid emulsion is given by the formula:

$$C_6H_5\ C_nH_{2n+1}$$

where n is an integer from 4 to 40, preferably 4 to 30 and most preferably 4 to 20.

The minimisation of branched alkyl benzene content is necessary to maximise biodegradability of the fluid.

Suitable compounds may for example be produced by the reaction of chlorinated paraffins or olefins with benzene in the presence of Friedel-Crafts catalyst, or the direct reaction of polyalphaolefin with benzene in the presence of hydrogen fluoride.

The resultant LAB may then be used as the external phase of an oil based emulsion at preferable oil/water ratios varying from 25/75 to 100/0.

Additives may be included in the fluid such as fluid loss additives, weighting agents such as barite and haematite, and speciality polymers.

Gelling agents, viscosity-controlling agents and water-soluble salts may also be present, and hydrocarbon oil and oil-soluble ester may be included

in the continuous phase of the emulsion.

The emulsified water content of the drilling fluid may contain dissolved salts such as sodium chloride, potassium chloride, calcium chloride, potassium acetate or any other soluble material added to adjust the resultant salt solution and drilling fluid density or to change the brine properties to enhance drilling.

The emulsifion may also contain natural brines such as sea water, aquifier fluids or may be fresh water of minimal dissolved salt content.

A component of the drilling fluid composition is preferably a surfactant which emulsifies the aqueous phase into the LAB and may typically be an organic acid, amide, ethoxylate, amine, phosphate, propoxylate or combination thereof.

Embodiments of the invention will be described by way of illustration in the following Examples.

The flash point of a series of liquid hydrocarbons has been measured by a closed cup technique in conjunction with an observed melting point (freezing temperature) for each material and kinematic viscosity at 40°C.

| Oil type | Flash Point/°C | Freezing Point/°C | Viscosity /cSt |
|---|---|---|---|
| Conventional "clean oils" | | | |
| BP 83HF* | 100 | -32 | 2.9 |
| Total HDF 200* | 110 | -30 | 3.2 |

| | | | |
|---|---|---|---|
| Alpha olefins (typical) | | | |
| $C_8$ | 15 | -102 | 0.7** |
| $C_{14}$ | 102 | -14 | 2.75** |
| $C_{18}$ | 150 | +17 | 3.3 |
| | | | |
| Linear alkyl benzene | | | |
| $C_8 - C_{10}$ | 123 | <-70 | 3 |
| $C_{10} - C_{12}$ | 130 | <-70 | 4 |
| $C_{11} - C_{13}$ | 135 | <-70 | 4 |

*Trade name

**Viscosity at 20°C

The above figures shown that LAB's exhibit very low freezing points and high flash points exceeding the performance of conventional "clean oils".

However, the precursor polyalphaolefins exhibit much higher freezing points at equivalent flash points which may cause problems in liquid handling under typical field conditions.

Drilling fluid emulsions in which linear alkyl benzene is used to replace the oil content of a conventional clean oil system have been prepared according to the procedure below.

An invert emulsion mud was prepared by mixing the following material quantities together on a Silverson blender at room temperature:

187.7 ml of hydrocarbon phase

12 g Kleemul 50 (emulsifier/surfactant

| | |
|---|---|
| | from BW Mud Ltd) |
| 6 g | Calcium oxide |
| 6 g | Emulhivis (treated organoclay viscosifier from BW Mud Ltd) |
| 144 ml | of a 25% solution of calcium chloride |

Once the drilling fluids had been prepared the mud rheologies and electrical stability were measured at 49°C, fluid loss monitored at 121°C and 500 psi differential.

The prepared fluids were then hot rolled at 121°C for 16 hours and mixed properties remeasured.

Linear alkyl benzenes obtained from Shell Chemicals under the trade names Dobane 83 and Dobane 103 were compared with a conventional "clean oil" from Shell branded as Shellsol DMA.

The above formulations result in 60/40 oil system of typical North Sea composition.

<u>COMPARATIVE EXAMPLE 1</u> using Shellsol DMA

| | |
|---|---|
| Apparent viscosity | 35 cP |
| Yield point | 9.6 Pa (20 lb/100 $ft^2$) |
| Plastic viscosity | 25 cP |
| Gel strengths | 5.3/5.8 Pa (11/12 lb/100 $ft^2$) |
| Fluid loss | 4.0 ml |
| Electrical stability | 279 V |

After hot rolling sample:

| | |
|---|---|
| Apparent viscosity | 36 cP |

| | |
|---|---|
| Yield point | 11.5 Pa (24 lb/100 $ft^2$) |
| Plastic viscosity | 24 cP |
| Gel strengths | 4.8/5.8 (10/12 lb/100 $ft^2$) |
| Fluid loss | 4.0 ml |
| Electrical stability | 309 V |

EXAMPLE 1

A drilling fluid was prepared using Dobane 83 a $C_8$ - $C_{13}$ linear alkyl benzene available from Shell Chemicals UK Ltd.

| | |
|---|---|
| Apparent viscosity | 53.5 cP |
| Yield point | 16.8 Pa (35 lb/100 $ft^2$) |
| Plastic viscosity | 36 cP |
| Gel strengths | 7.2/6.7 Pa (15/14 lb/100 $ft^2$) |
| Fluid loss | 2.0 ml |
| Electrical stability | 166 V |

After hot rolling sample:

| | |
|---|---|
| Apparent viscosity | 62 cP |
| Yield point | 21.1 Pa (44 lb/100$ft^2$) |
| Plastic viscosity | 40 cP |
| Gel strengths | 9.1/10.1 Pa (19/21 lb/100 $ft^2$) |
| Fluid loss | 2.2 ml |
| Electrical stability | 495 V |

EXAMPLE 2

A drilling fluid was prepared using Dobane 103 a $C_{10}$ - $C_{13}$ linear alkyl benzene available from Shell Chemicals UK Ltd.

| | |
|---|---|
| Apparent viscosity | 62 cP |

| | |
|---|---|
| Yield point | 21.1 Pa (44 lb/100 $ft^2$) |
| Plastic viscosity | 40 cP |
| Gel strengths | 9.1/8.6 Pa (19/18 lb/100 $ft^2$) |
| Fluid loss | 2.0 ml |
| Electrical stability | 169 V |

After hot rolling sample:

| | |
|---|---|
| Apparent viscosity | 75 cP |
| Yield point | 25.9 Pa (54 lb/100 $ft^2$) |
| Plastic viscosity | 48 cP |
| Gel strengths | 12.5/13.4 Pa (26/28 lb/100 $ft^2$) |
| Fluid loss | 2.4 ml |
| Electrical stability | 612 V |

COMPARATIVE EXAMPLE 2

A drilling fluid of 50/50 Shellsol DMA (prior art)/water ratio was prepared by blending the following materials on a Silverson emulsifier:

| | |
|---|---|
| 230 ml | Shellsol DMA |
| 19.9 g | Kleemul 50 |
| 8.3 g | Lime |
| 4.95 g | Emulhivis |
| 232 ml | Water |
| 46.35 g | Calcium chloride |

The resultant emulsion properties were:

| | |
|---|---|
| Apparent viscosity | 32.5 cP |
| Yield point | 6.2 Pa (13 lb/100 $ft^2$) |
| Plastic viscosity | 26 cP |
| Gel strengths | 3.4/3.4 Pa (7/7 lb/100 $ft^2$) |
| Electrical stability | 129 V |

It is clear that in comparison with Comparative Example 1 the electrical stability value and hence emulsion stability of the drilling fluid is much reduced.

EXAMPLE 3

A drilling fluid according to the formulation given in Comparative Example 2 was produced using Dobane 83 in place of Shellsol DMA.

The resultant emulsion properties were:

| | |
|---|---|
| Apparent viscosity (49°C) | 65 cP |
| Yield point | 21.1 Pa (44 lb/100 $ft^2$) |
| Plastic viscosity | 43 cP |
| Gel strengths | 8.6/8.6 Pa (18/18 lb/100 $ft^2$) |
| Electrical stability | 192 V |

A comparison of the properties of this 50/50 emulsion drilling fluid with the fluid produced in Example 1 at a 60/40 ratio demonstrates no loss in electrical stability. That is, the linear alkyl benzene results in a high stability emulsion although the water content has increased.

EXAMPLE 4

A drilling fluid according to the formulation in Comparative Example 2 was produced using Dobane 103 in place of Shellsol DMA.

The resultant emulsion properties were:

| | |
|---|---|
| Apparent viscosity (120°F) | 75.5 cP |

| | |
|---|---|
| Yield point | 24.5 Pa (51 lb/100 $ft^2$) |
| Plastic viscosity | 50 cP |
| Gel strengths | 10.1/11.5 Pa (21/24 lb/100 $ft^2$) |
| Electrical stability | 153 V |

In comparison with Example 2 using a higher 60/40 oil/water ratio the 50/50 emulsion produced shows an emulsion electrical stability of similar value, that is of enhanced performance compared to the prior art clean oil system of Comparative Example 2.

Linear alkyl benzene therefore demonstrates improved stability in high water content drilling fluids and produces fluids of satisfactory rheology, fluid loss and thermal stability suitable for drilling operations.

EXAMPLE 5

A drilling fluid was prepared using PETRELAB P 400, a linear alkyl benzene of $C_{10}$ - $C_{12}$ alkyl side chain produced by Petroquimica Expanola (PETRESA) of Spain and commercially available as a detergent alkylate.

The formulation was compared against the base oil BP 83HF, a conventional clean oil produced by BP Chemicals.

Fluids were mixed using a laboratory blender to give a 50/50 system of the following composition:

| | |
|---|---|
| 109.1 ml | P 400 or BP 83HF |
| 12 g | Kleemul 50 surfactant emulsifier |
| 6 g | lime |
| 2 g | Perchem DMB organoclay gellant from Akzo Chemicals |

| | |
|---|---|
| 128.2 ml | water |
| 56.2 g | calcium chloride (82-85%) |
| | barite to give a density of 1.43 (12 ppg) |

Each fluid was tested for rheology at 49°C and then hot rolled at 121°C for 16 hours before remeasuring properties.

| Oil Phase | Akyl benzene P 400 | | Clean Oil BP 83HF | |
|---|---|---|---|---|
| | BHR | AHR | BHR | AHR |
| Apparent viscosity/cP | 92 | 93 | 65 | 79 |
| Yield point/Pa | 12.5 | 27.8 | 10.6 | 17.3 |
| Plastic viscosity/cP | 79 | 64 | 54 | 61 |
| Gels/Pa | 4.8/8.2 | 4.8/9.1 | 2.9/4.8 | 3.8/6.2 |
| Electrical stability/V | 418 | 580 | 460 | 561 |
| Fluid loss at: | | | | |
| 500 psi/121°C | - | 4.4 ml | - | 7.6 ml |

The use of an alkylbenzene P 400 gives improved rheology (increased yield point and gel strengths) and improved fluid loss control.

Claims

1 Drilling fluid comprising an emulsion whose continuous phase comprises a linear alkyl benzene.

2 Drilling fluid according to Claim 1, in which the linear alkyl benzene contains an alkyl group having from 4 to 40 carbon atoms.

3 Drilling fluid according to Claim 1, in which the linear alkyl benzene contains an alkyl group having from 4 to 30 carbon atoms.

4 Drilling fluid according to Claim 1, in which the linear alkyl benzene contains an alkyl group having from 4 to 20 carbon atoms.

5 Drilling fluid according to any one of the preceding Claims, in which the ratio of total linear alkyl benzene to water in the emulsion is from 25/75 to 100/0 by volume.

6 Drilling fluid according to any one of the preceding Claims, containing also a surface active agent.

7 Drilling fluid according to any one of the preceding Claims, containing also a gelling agent.

8 Drilling fluid according to Claim 7, in which the gelling agent is selected from clay, modified organoclays, polymers and resins.

9 Drilling fluid according to any one of the preceding Claims, containing also a weighting

agent.

10 Drilling fluid according to Claim 9 , wherein the weighting agent is barite.

11 Drilling fluid according to any one of the preceding claims, containing also a water-soluble salt.

12 Drilling fluid according to any one of the preceding claims, containing also a material which controls fluid loss.

13 Drilling fluid according to any one of the preceding claims, containing also a viscosity-controlling agent.

14 Drilling fluid according to any one of the preceding claims, containing also a hydrocarbon oil in the continuous phase of the emulsion.

15 Drilling fluid according to any one of the preceding Claims, containing also an oil-soluble ester in the continuous phase of the emulsion.

16 Drilling fluid substantially as hereinbefore described with reference to any one of Examples 1 to 5.

**Patents Act 1977**
**Examiner's report to the Comptroller under Section 17 (The Search Report)**

Application number

GB 9215569.6

**Relevant Technical fields**

(i) UK Cl (Edition K ) E1F (FGP)

(ii) Int Cl (Edition 5 ) C09K

**Databases (see over)**

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI

Search Examiner

D B PEPPER

Date of Search

25 AUGUST 1992

Documents considered relevant following a search in respect of claims 1-16

| Category (see over) | Identity of document and relevant passages | Relevant to claim(s) |
|---|---|---|
| | NONE | |

SF2(p)

HD - doc99\fil000196

| Category | Identity of document and relevant passages | Rele t to claim(s) |
|---|---|---|
| | | |

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